

Patent claims:

1. Process for the treatment of leathers or skins, pretanned with dialdehydes and retanned with organic tanning agents, with anionic reagents in an aqueous liquor, in which
  - a) either an anionic reagent together with at least one organic polyamine having at least three amino groups in the molecule, or mixtures or reaction products (1) of such polyamines with (2) at least one alkylsilane having organic oxy radicals bonded to the silicon atom and a functional group bonded to the alkyl group so that said reaction products have at least two free amino groups in the molecule, said functional group forming covalently bonded bridging groups with an amino group of the polyamine, are added to the liquor and allowed to act on the leather,
  - b) or the leather is first treated with anionic reagents and then, in the same or a fresh liquor, at least one organic polyamine having at least three amino groups in the molecule, or mixtures or reaction products (1) of such polyamines with (2) at least one alkylsilane having organic oxy radicals bonded to the silicon atom and a functional group bonded to the alkyl group so that said reaction products have at least two free amino groups in the molecule, said functional group forming a covalently bonded bridging group with an amino group of the polyamine, is or are allowed to act on the treated material,
  - c) or the leather is first treated with an organic polyamine having at least three amino groups in the molecule, or mixtures or reaction products (1) of such polyamines with (2) at least one alkylsilane having organic oxy radicals bonded to the silicon atom and a functional group bonded to the alkyl group so that said reaction products have at least two free amino groups in the molecule, said functional group forming a covalently bonded bridging group with an amino group of the polyamine, and the anionic reagents are then allowed to act on the treated material in the same or a fresh liquor.
2. Process according to Claim 1, characterized in that the anionic reagents are fatliquoring agents, water repellents, organic tanning and retanning agents or dyes which have at least one acidic group.
3. Process according to Claim 1, characterized in that the anionic auxiliaries are used in an amount of from 0.1 to 30% by weight, based on the shaved weight of the leather or the skins.

4. Process according to Claim 1, characterized in that the auxiliary is an anionic dye.

5. Process according to Claim 1, characterized in that the polyamines are low molecular weight, oligomeric or polymeric compounds which are soluble in polar solvents and also in water.

6. Process according to Claim 1, characterized in that the low molecular weight polyamines are saturated or unsaturated, open-chain, mono- or polycyclic compounds which contain 6 to 30 C atoms.

7. Process according to Claim 1, characterized in that the polyamines are oligomers or polymers in which the amino groups are bonded either directly or via a bridging group to the polymer backbone or in the polymer backbone.

8. Process according to Claim 7, characterized in that the oligomers contain from 3 to 100, preferably from 3 to 50 and particularly preferably from 3 to 30 and the polymers more than 100 and up to about 28 000 identical or different monomer units.

9. Process according to Claim 7, characterized in that the oligomers and polymers contain at least one repeating structural element of the formula II and optionally at least one repeating structural element of the formula III



in which

R<sub>1</sub> is H or C<sub>1</sub>-C<sub>4</sub>alkyl,

R<sub>2</sub> is H or methyl,

$R_3$  is H,  $C_1$ - $C_{17}$ alkyl, phenyl, methylphenyl, pyrrolidinyl, Cl,  $-O$ - $C_1$ - $C_4$ alkyl,  $-O$ -(CO)- $C_1$ - $C_4$ alkyl,  $-C(O)$ -OR<sub>4</sub> or  $-C(O)$ -NR<sub>5</sub>R<sub>6</sub>,

$R_4$  is H or  $C_1$ - $C_{18}$ alkyl and

$R_5$  and  $R_6$ , independently of one another, are H or  $C_1$ - $C_4$ alkyl.

10. Process according to Claim 7, characterized in that the oligomers and polymers are adducts of organic diamines and aziridine or a polyethylenamine.

11. Process according to Claim 10, characterized in that the adducts contain repeating structural elements of the formula IV and optionally repeating structural elements of the formula V



terminal groups  $R_8$  being bonded to the ends of the chains, in which

$R_7$  is  $C_2$ - $C_{12}$ alkylene,  $C_5$ - $C_8$ cycloalkylene or  $C_6$ - $C_{10}$ arylene,

$R_8$  is hydrogen,  $C_1$ - $C_{18}$ alkoxy or  $C_1$ - $C_{18}$ alkylamino and

the  $R_{16}$ , independently of one another, are H or  $C_1$ - $C_4$ alkyl.

12. Process according to Claim 11, characterized in that the adducts are oligomers having 3 to 15 structural elements of the formula IV and optionally repeating structural elements of the formula V.

13. Process according to Claim 11, characterized in that the content of repeating structural elements of the formula IV is from 50 to 100 mol% and the content of repeating structural elements of the formula V is from 50 to 0 mol%.

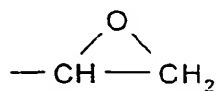
14. Process according to Claim 1, characterized in that an alkylsilane having organic oxy radicals bonded to the silicon atom and a functional group bonded to the alkyl group is additionally concomitantly used, either as a mixture with the polyamine or as a reaction product with the polyamine, the amino groups of the polyamine and the functional group together forming a covalently bonded bridging group.

15. Process according to Claim 14, characterized in that the functional silane corresponds to the formula VI,



in which

$R_{13}$  is  $C_1$ - $C_4$ alkyl and in particular methyl,  $R_{14}$  is  $-(CH_2)_3-O-CH_2-$  and  $X_1$  is an epoxide group of the formula



or  $R_{14}$  is  $C_2$ - $C_6$ alkylene and  $X_1$  is  $-NCO$  or  $-C(O)OR_{15}$ , in which  $R_{15}$  is hydrogen or  $C_1$ - $C_4$ alkyl.

16. Process according to Claim 15, characterized in that the amount of functional alkylsilanes in the composition with the polyamine is preferably from 1 to 60% by weight, based on the total amount of polyamine and functional alkylsilane.

17. Process according to Claim 1, characterized in that the polyamine or the mixture or reaction product of polyamine and alkylsilane is used in an amount of from 0.1 to 30% by weight, based on the shaved weight of the fibrous material.

18. Process according to Claim 1, which is carried out at from room temperature to  $60^\circ\text{C}$ .

19. Composition comprising (a) at least one low molecular weight, oligomeric or polymeric polyamine having at least 3 amino groups and (b) at least one alkylsilane having organic oxy radicals bonded to the silicon atom and a functional group bonded to the alkyl group, said functional group being capable of forming a covalently bonded bridging group with an amino group of the polyamine.

20. Composition according to Claim 19, characterized in that the amount of functional alkylsilanes in the composition is from 1 to 60% by weight, based on the total amount of polyamine and functional alkylsilane.

21. Reaction product obtainable by reacting (1) at least one organic polyamine which has at least three amino groups in the molecule with (2) at least one alkylsilane having organic oxy radicals bonded to the silicon atom and a functional group bonded to the alkyl group, so that

said reaction product has on average at least two free amino groups in the molecule, said functional group forming a covalently bonded bridging group with an amino group of the polyamine, with the exception of 4,7,10-triazadecyl-1-trimethoxysilane.

22. Reaction product according to Claim 21, characterized in that the amount of functional alkylsilanes in the reaction product is from 1 to 60% by weight, based on the total amount of polyamine and functional alkylsilane.

23. Reaction product according to Claim 22, which is an oligomer or polymer having structural elements of the formula VII and optionally structural elements of the formulae VIII and IX



in which

R<sub>16</sub> is H or C<sub>1</sub>-C<sub>4</sub>alkyl,

R<sub>17</sub> is C<sub>2</sub>-C<sub>6</sub>alkylene,

R<sub>18</sub> is C<sub>1</sub>-C<sub>4</sub>alkyl,

X<sub>2</sub> is a direct bond, -C(O)-, -C(O)-O-, -C(O)-NH-, -CH<sub>2</sub>CH(OH)CH<sub>2</sub>-O- or -CH(CH<sub>2</sub>OH)CH<sub>2</sub>-O-,

R<sub>19</sub> is H or methyl,

R<sub>20</sub> is H, C<sub>1</sub>-C<sub>17</sub>alkyl, phenyl, methylphenyl, pyrrolidiny, Cl, -O-C<sub>1</sub>-C<sub>4</sub>alkyl, -O-(CO)-C<sub>1</sub>-C<sub>4</sub>alkyl, -C(O)-OR<sub>21</sub> or -C(O)-NR<sub>22</sub>R<sub>23</sub>,

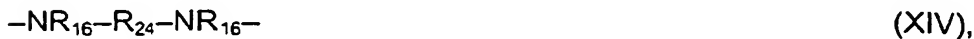
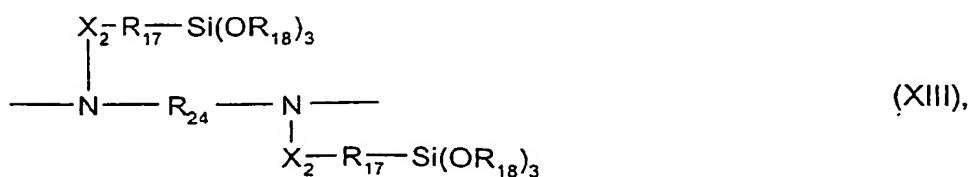
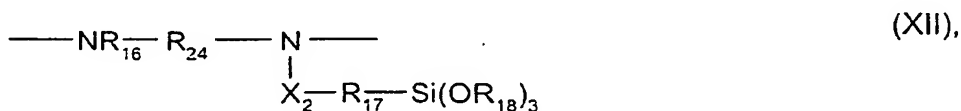
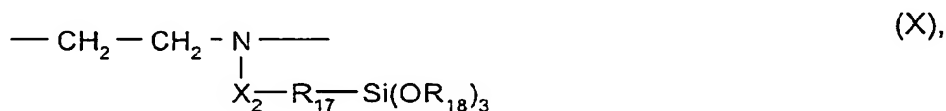
R<sub>21</sub> is H or C<sub>1</sub>-C<sub>18</sub>alkyl, and

R<sub>22</sub> and R<sub>23</sub>, independently of one another, are H or C<sub>1</sub>-C<sub>4</sub>alkyl.

24. Reaction product according to Claim 23, characterized in that the amount of structural elements of the formula VII is from 0.1 to 100 mol% and the amount of structural elements of the formula VIII is from 0 to 99.9 mol%, based on 1 mol of an oligomer or polymer.

25. Reaction product according to Claim 23, characterized in that the structural elements of the formula IX replace up to 80 mol% of the structural elements of the formulae VII and VIII.

26. Reaction product according to Claim 21, which is an oligomer or polymer having repeating structural elements of the formula X and optionally repeating structural elements of the formulae XI, XII, XIII and/or XIV



terminal groups R<sub>25</sub> being bonded to the ends of the oligomer and polymer chains, in which the R<sub>16</sub>, independently of one another, are H or C<sub>1</sub>-C<sub>4</sub>alkyl,

R<sub>17</sub> is C<sub>2</sub>-C<sub>6</sub>alkylene,

R<sub>18</sub> is C<sub>1</sub>-C<sub>4</sub>alkyl,

X<sub>2</sub> is a direct bond, -C(O)-, -C(O)-O-, -C(O)-NH-, -CH<sub>2</sub>CH(OH)CH<sub>2</sub>-O- or CH(CH<sub>2</sub>OH)CH<sub>2</sub>-O-,

R<sub>24</sub> is C<sub>2</sub>-C<sub>12</sub>alkylene, C<sub>5</sub>-C<sub>6</sub>cycloalkylene or C<sub>6</sub>-C<sub>10</sub>arylene and

R<sub>25</sub> is hydrogen, C<sub>1</sub>-C<sub>18</sub>alkoxy, C<sub>1</sub>-C<sub>18</sub>alkylamino or the group -X<sub>2</sub>-R<sub>17</sub>-Si(OR<sub>18</sub>)<sub>3</sub>.

27. Reaction product according to Claim 26, characterized in that R<sub>16</sub> is methyl and preferably H, X<sub>2</sub> is -C(O)-NH- and R<sub>17</sub> is 1,3-propylene, or -X<sub>2</sub>-R<sub>17</sub>- is -CH<sub>2</sub>CH(OH)CH<sub>2</sub>-O-(CH<sub>2</sub>)<sub>3</sub>, R<sub>18</sub> is C<sub>1</sub>-C<sub>4</sub>alkoxy and preferably methyl, R<sub>24</sub> is C<sub>2</sub>-C<sub>6</sub>alkylene and in particular ethylene, and R<sub>25</sub> is hydrogen or the group -X<sub>2</sub>-R<sub>17</sub>-Si(OR<sub>18</sub>)<sub>3</sub>.

28. Reaction product according to Claim 26, characterized in that the amount of structural elements with bonded alkylsilanes is from 0.1 to 30 mol%, based on 1 mol of an oligomer or polymer.

29. Reaction product according to Claim 26, which is an oligomeric adduct having from 3 to 100 structural elements of the formulae X, XII and/or XIII and optionally structural elements of the formulae XI and XIV.

30. Reaction product according to Claim 29, characterized in that the content of repeating structural elements of the formulae X, XII and/or XIII is from 1 to 100 mol% and the content of repeating structural elements of the formulae XI and XIV is from 99 to 0 mol%, based on 1 mol of the oligomer with inclusion of the terminal groups.

31. Composition comprising (1a) at least one unmodified organic polyamine having at least three free amino groups, (1b) at least one reaction product according to Claim 21 or a composition according to Claim 19, (2) a carrier for the components (1a) and (1b), and (3) optionally further additives.

32. Composition according to Claim 31, characterized in that the amount of components (1a) or (1b) is from 0.1 to 80% by weight, based on the composition.

33. Composition according to Claim 31, characterized in that the carrier is selected from organic solvents or water with addition of an acid.

34. Use of an organic polyamine having at least three amino groups, of a composition according to Claim 19 or 31 or of a reaction product according to Claim 21 as an auxiliary in the finishing of leathers and skins, pretanned with dialdehydes and retanned with organic tanning agents, with anionic auxiliaries.